Supplementary Information for:

Hydrogen Evolution Characteristics of Ni–Mo-Coated Radial Junction n^+p Silicon Microwire Array Photocathodes

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Comparing Galvanostatic and Potentiostatic deposition of Ni–Mo

Figure S1 shows the *J-E* performance for two nominally identical radial n^+-p junction SiMW electrodes with Ni–Mo deposited by galvanostatic (red) and potentiostatic (blue) conditions, respectively. The electrodes were made without any scattering particles, and thus produced lower J_{sc} values then the champion devices.

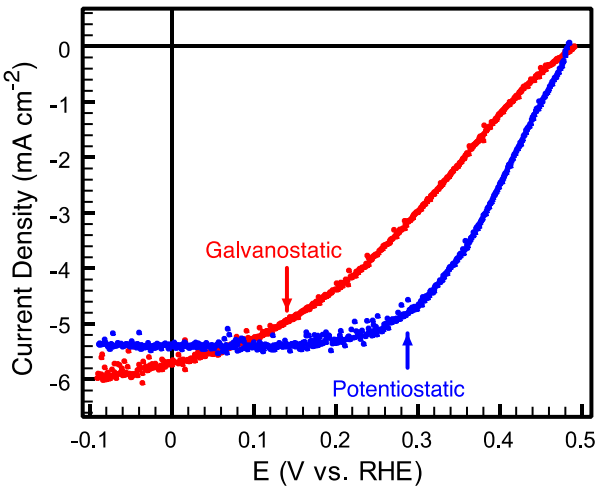

Figure S1: *J-E* data for n^+p-Si MW array photocathodes measured in H_2-purged pH 4.5 KHP buffer under ELH-type solar illumination. The data in red are for Ni–Mo deposited under galvanostatic conditions, and the data in blue for Ni–Mo deposited potentiostatically. The *J-E* data are referenced to the reversible hydrogen evolution potential in the solution ($E(H^+/H_2)$ = -0.51 V vs. SCE).

The effect of electrolyte on catalytic activity

Figure S2 shows a comparison of H_2 generation at a Pt electrode in 0.5 M H_2SO_4 and pH 4.5 KHP buffer. The onset of catalytic activity is not as rapid at neutral pH, due to the change in mechanism of the HER at the different pH conditions.

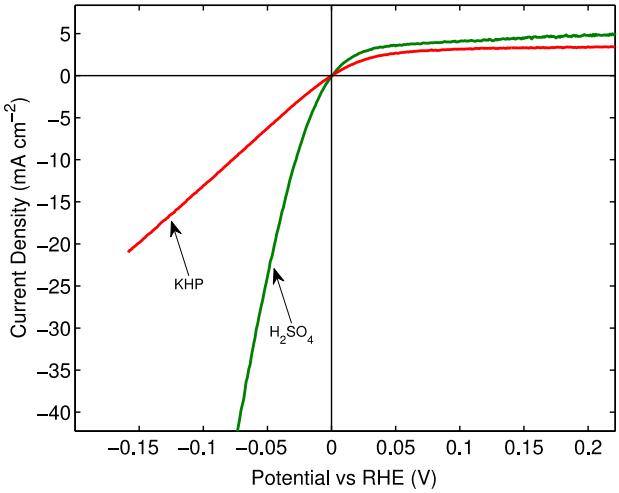

Figure S2: Comparison of Pt electrode in pH 4.5 KHP and 0.5 M H_2SO_4 (pH=0). Data were collected using linear sweep voltammetry at 20 mV s^{-1}. Prior to data collection, the Pt working electrode was repeatedly cycled between -0.2 V and +1.2 V versus RHE to clean the Pt surface.